

PATENT SPECIFICATION

676.011



Date of Application and filing Complete Specification: April 19, 1949.

No. 10398/49.

Application made in United States of America on April 19, 1948.

Complete Specification Published: July 23, 1952.

Index at acceptance:—Classes 2(iii), H; 2(v), R2c(4:5:6:8:12:16), R2(h:m1), R2p(1:2:4), R2tl, R19c(4:5:6:8:12:16), R19(m:p:t1), R22c(4:5:6:8:12:16), R22(m:p), R22t(1:2); and 96, B(2b:13f:14f).

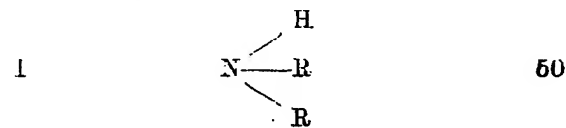
COMPLETE SPECIFICATION

Modified Aminoplasts and Products Prepared therefrom

We, BRITISH INDUSTRIAL PLASTICS LIMITED, a company organised under the laws of Great Britain, of 1, Argyll Street, London, W.1, assignees of HENRY PETER WOHNISIEDLER, of 66, Five Mile River Road, Darien, Connecticut, United States of America, EDWARD L. KROPA, of 7, Rockmere Avenue, Old Greenwich, Connecticut, United States of America, and WALTER MORELAND THOMAS, of 161, South Street, Stamford, Connecticut, United States of America, all citizens of the United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to new and useful compositions having properties that render them particularly useful in the plastics, coating, laminating and other arts, to products prepared therefrom and to methods of producing such compositions and products. More particularly the invention is concerned with compositions of matter and products comprising a modified aminoplast, specifically a modified, heat-curable (thermosetting) or a heat-cured (thermoset), resinous or other product of reaction of ingredients comprising (a) an aldehyde, e.g. formaldehyde, and (b) a monomeric amidogen compound, which is herein defined as a monomeric compound containing not less than two amino or amido groupings each having at least one hydrogen atom attached to the nitrogen atom, e.g., urea, thiourea, melamine, methylurea, diethylmelamine, guanidine, dicyandiamide, guanylurea, biguanide or guanylmelamine. In accordance with the present invention such reaction products are modified with a nitrogenous compound which is different from the compound of (b) and which is a member of the class consisting of (1) linear polymeric reaction products of (A)

epsilon-caprolactam and (B) a compound represented by the general formula



where R represents hydrogen, an alkyl radical or a monohydroxyalkyl radical, the ingredients of (A) and (B) being employed in the ratio of 1 mole of the former to not less than 1 mole of the latter, (2) aldehyde-reaction (e.g., formaldehyde-reaction) products of (1), and (3) mixture of (1) and (2). The scope of the invention also includes methods of preparing such compositions and products, e.g., a post-formable laminated article comprising superimposed sheets of fibrous material impregnated and bonded together with a modified aminoplast of the kind briefly described above.

The ingredients used in the preparation of the linear polymeric reaction products referred to under (1) of the preceding paragraph may be employed in the ratio of 1 mole of epsilon-caprolactam to from 1 mole to 20 moles of a compound or mixture of compounds of the kind embraced by Formula I, e.g., anhydrous ammonia; a monoalkylamine such, for instance, as *n*-butylamine or *n*-decylamine; a dialkylamine, for example, dihexylamine or dioctylamine; a monoalkanolamine such, for instance, as ethanolamine or isopropanolamine; or a dialkanolamine, for example, diethanolamine or di-*n*-butanolamine. Among the linear polymeric reaction products which may be used in carrying the present invention into effect, are those which are composed substantially completely of the said linear reaction products and which have an average molecular weight of not more than 2000, more particularly those having an average

number of caprolactam units per molecule ranging from a little above 2 (e.g., 2.5), generally at least 3 or 4, to 16.

Illustrative examples of alkyl radicals which R in formula I may represent are: methyl, ethyl, propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *tert*-butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl to octadecyl, inclusive, including cycloalkyl (e.g., cyclohexyl). Illustrative examples of monohydroxyalkyl radicals which R in Formula I may represent are: monohydroxy-methyl, -ethyl, -propyl, -isopropyl, -*n*-butyl, -isobutyl, -*sec*-butyl, -*tert*-butyl, -amyl, -hexyl, -heptyl, -octyl, -nonyl, -decyl to -octadecyl, inclusive, including monohydroxycycloalkyl (e.g., monohydroxycyclohexyl).

In the commercial utilisation of aminoplasts in the plastics, coating and laminating arts, it is frequently necessary to modify the heat-curable (heat-convertible) or potentially heat-curable aminoplast by incorporating therein a plasticiser or softener so that the aminoplast will flow properly in the particular coating or laminating composition or, in the case of thermosetting aminoplast moulding compositions, will show good plastic flow characteristics during moulding. For example, if improper or insufficient plastic flow occurs during the moulding operation, the molded articles may show streaked or wavy surfaces. Furthermore, if the plasticity of the moulding composition is not sufficient, lack of physical homogeneity as the result of incompletely knitted granules often characterises the mouldings, especially very large mouldings.

In filled (e.g., cellulose-filled) moulding compositions it is also important that the plasticiser be compatible with both the cellulose and the aminoplast, e.g., a melamine-formaldehyde resin, so as to obtain moulded articles having optimum dimensional stability and resistance to cracking around inserts. In impregnating, coating and laminating compositions wherein the aminoplast is utilised in the form of a solution thereof, it is also important that the plasticiser or softener for the aminoplast be soluble in the same solvent in which the aminoplast is dissolved, and for economic reasons it is also desirable that this solvent be relatively inexpensive.

There has also long been a need in the laminating art for a light-coloured laminate wherein the binder for the laminae was such as to impart post-formability characteristics to the laminated sheet article. For example, whereas many plasticised melamine-formaldehyde resinous compositions are suitable for a

wide variety of service applications, to the best of our knowledge and belief none of the compositions of this kind, which were known or suggested prior to our invention, have been such that a laminated article in which such prior binders were used could be satisfactorily post-formed to a desired shape, e.g., into the form of a helmet liner.

In the production of, for example, laminated structures, e.g., paper- and canvas-filled laminates, it is also important that the aminoplast binder impart optimum flexural-strength characteristics to the laminate, and that it be possible to subject the laminated article to sawing, punching, drilling and other fabrication operations without cracking, chipping, breaking or other damage thereto. These properties and, in some cases, workability are also desirable in moulded aminoplast articles wherein the filler is of the finely divided type, e.g., alpha-cellulose. It is apparent, therefore, that in many cases it is desirable that the modifier of the aminoplast be able to toughen the cured aminoplast so that it will be able effectively to withstand sudden shocks and strains. In numerous instances such a toughening agent advantageously is one which also imparts a plasticising or softening action to the heat-curable aminoplast as it assumes its ultimate form or shape. Generally, plasticisers and toughening agents perform several functions in a moulding composition. The lower-molecular-weight derivatives generally promote flow and increase the plasticity of the product whereas the higher-molecular weight components act as toughening agents.

From the foregoing it will be seen that in the utilisation of plasticised aminoplasts in moulding, impregnating, coating, laminating, casting and other applications, it is important that the plasticiser or softener and/or toughening agent have certain characteristics. The particular characteristics or combination of characteristics desired in the plasticiser obviously will vary to some extent depending upon the particular service application of the plasticised aminoplast, but the following are usually necessary requisites:

The plasticiser should improve the flow of the heat-curable aminoplast, or moulding or other composition containing the same, during moulding or other use preferably without retarding the curing of the resin at the curing temperature. It should be compatible with the aminoplast both at normal and at elevated temperatures and should not "bleed" from the cured aminoplast or product or article comprising the same. It should not dis-

colour, or impart an odour to, or lessen the water resistance, electrical properties, mechanical strength and other useful properties of the cured aminoplast or composition or body containing the same. The most desirable modifier, of course, is one which improves the physical properties of the cured aminoplast, as by toughening it, or makes the modified aminoplast suitable for fields of utility for which the unmodified aminoplast is unsuited.

From the foregoing it will be seen that the number of plasticisers (softeners) and/or toughening agents for heat-curable and heat-cured aminoplasts of the kind described in the first paragraph of this specification are relatively few. Urea and various substituted ureas, aniline and toluene sulphonamides are among those which heretofore have been used or suggested for use as plasticisers for aminoplasts. Various other nitrogen-containing compounds also have been suggested as plasticisers for heat-curable and heat-cured aminoplasts. In general, these prior plasticisers either have not been entirely satisfactory, so that the plasticised compositions had only limited utility, or have been so relatively expensive as to prohibit their use. Furthermore, in many cases the improvement in plasticity or softening was attained only at the sacrifice of some other useful property of the aminoplast.

The linear polymers, used in the present invention, especially those having an average molecular weight of not more than 1200, more particularly those with an average molecular weight within the range of 400 or 450 to 1000, effectively plasticise the heat-convertible amidogen-aldehyde aminoplast so that it has good flow characteristics during moulding and in other uses. Furthermore, the curing of the heat-curable aminoplast during moulding proceeds satisfactorily. Also, the aminoplast is plasticised without any substantial decrease in the other valuable properties of the heat-hardened aminoplast, such as resistance to cracking around inserts, dielectric strength, surface appearance, colour, odour and mechanical strength. In fact, a definite improvement in some properties is obtained, for instance, less after-shrinkage of the moulded article; less cracking or tendency to crack around metal inserts in molded articles; and improved flexural strength. Furthermore, the linear polymers are soluble in cheap solvents, e.g., a mixture of water and alcohol, so that liquid compositions comprising a solution of a plasticised aminoplast can be prepared. These liquid compositions of our invention are especially suitable for use

in making post-formable laminated articles comprising a cured, plasticised aminoplast binder, for which latter there has long been a need in the laminating art.

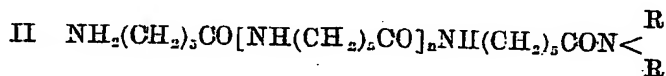
It was quite surprising and unexpected that linear polymeric materials of the kind described above would be able to coact with amidogen-aldehyde aminoplasts, such as are employed in practising our invention, with the result that the modified aminoplasts are different in kind (as evidenced by their difference in properties) from the linear polymeric material and the amidogen-aldehyde aminoplast which are combined to produce the new compositions and products of the present invention. It may here be noted that all of the linear polymers used in practising our invention are aldehyde-reactable and can be inter-condensed into the amidogen-aldehyde aminoplast; or, the linear polymer and/or an aldehyde-reaction product thereof otherwise (e.g., during a milling, blending or other operation) can be caused to become chemically bound in the aminoplast and compatible with it. Since the linear polymer is bound in the aminoplast and integral with it, there is no tendency of the polymer to separate from the aminoplast or for it to cause poor "knitting" of the resin component in, for instance, a filled aminoplast. Furthermore, larger amounts of linear polymer can be tolerated as a modifier of the aminoplast than usually has been possible with plasticised aminoplasts wherein the plasticiser is non-reactive or substantially non-reactive with the aminoplast. These results were quite surprising and unexpected, since in no way could it have been predicted from the properties of the afore-mentioned linear polymers or from the properties of amidogen-aldehyde aminoplasts that the linear polymers not only would be able effectively to plasticise the heat-curable aminoplast but would do this without sacrifice of the useful properties of the cured aminoplast.

The reaction products of epsilon-caprolactam and a compound of the kind embraced by Formula I, using molar ratios of reactants such as have been mentioned hereinbefore, are polymeric materials having non-fibre-forming characteristics. More particularly they comprise a mixture of linear polymers having an average molecular weight not higher than 2000, usually an average molecular weight within the range of 300 or 350 to 1000 or 1400. They are normally solids which liquefy under heat. Depending upon the particular compound which is reacted with the epsilon-caprolactam and the extent, if any, to which the

product has been purified, they vary from waxy or wax-like solids to fine powders or easily friable solids. Some of the products are soluble in hot water, in alcohol (ethyl alcohol), and in mixtures of alcohol and water, but are insoluble in benzene. In general, their intrinsic viscosities are relatively low, usually being within the range of 0.05 to 0.3 or 0.35. Products

having intrinsic viscosities within the 10 range of, for example, 0.05—0.1 to 0.2—0.25 may be used in plasticising amidogen - aldehyde aminoplasts as herein described.

The polymeric reaction products as 15 ordinarily produced may be represented by the following general formula:

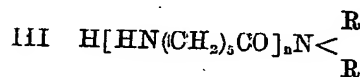


wherein n represents a number from 1 to 16, inclusive, that is to say, n has an average value between 1 and 16, inclusive, and R has the same meaning as given above with reference to Formula I. In all cases the initial reaction product comprises a mixture of polymers. The mixture may contain a small amount of the dimer in which case n in the above formula would be 0. The crude reaction product containing a mixture of linear polymers may be fractionated by the use of particular solvents or mixtures of solvents to obtain fractions in which the polymers are present within a narrower limit of molecular weights.

Of the linear polymeric materials represented by Formula II we prefer to use, in carrying the present invention into effect, those wherein n has an average value between 1 and 7, optimum results usually being obtained in most applications when the average value of n is between 2 and 3. Such polymers, especially those of lower molecular weight, are readily soluble in,

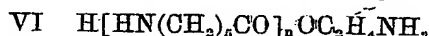
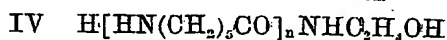
for example, alcohol or in mixtures of water and alcohol.

As will be apparent to those skilled in the art, the linear polymers represented by Formula II also may be represented by the general formula



wherein n has an average value between 3 and 18, inclusive, preferably between 3 and 9, inclusive, and R has the same meaning as given above with reference to Formula I. The dimer is represented when n is 2.

When epsilon - caprolactam and an alkanolamine, e.g., monoethanolamine, are caused to react there is a possibility that the linear polymeric reaction products may be polymers corresponding to one or another of the following formulae, taking monoethanolamine as illustrative of the alkanol-amine reactant employed:



wherein n has the same meaning as given above with reference to Formula III. However, since both unreacted ethanolamine and unreacted epsilon-caprolactam are present in the reaction mass at the end of the reaction period, this constitutes rather persuasive evidence that the polymeric reaction product is predominantly, if not solely or substantially completely, a polymer of the kind represented by Formula IV.

Illustrative examples of amidogen-aldehyde aminoplasts which may be modified with the linear polymeric material herein described are aminotriazine-aldehyde resins (e.g., melamine-formaldehyde resins), urea-aldehyde resins (e.g., urea-formaldehyde resins), thiourea-aldehyde resins (e.g., thiourea-

formaldehyde resins), urea-aminotriazine-aldehyde resins (e.g., urea-melamine-formaldehyde resins), aminodiazine-aldehyde resins (e.g., aminodiazine-formaldehyde resins), protein-aldehyde resins (e.g., casein-formaldehyde resins), resinous condensation products of an aldehyde, e.g., formaldehyde, with a polyamide of a polycarboxylic acid, e.g., maleic diamide, succinic diamide, fumaric diamide, itaconic diamide, phthalic diamide or citric triamide.

The amount of linear polymeric material of the kind used in practicing our invention and which is incorporated into the amidogen-aldehyde aminoplast to modify, specifically plasticise or soften and/or toughen, the latter may be varied as desired or as conditions may require.

In some cases, only a relatively small amount may be required, e.g., from 1% to 3 or 4% by weight of the combined amount of modifier and aminoplast.

5 Ordinarily, however, the linear polymeric modifier constitutes, by weight, from 5% to 50%, more particularly from 5—10% to 30—40%, of the combined amount of modifier and aminoplast. For some
10 applications, for example where the thermoplastic or semi-thermoplastic properties of the composition are not objectionable, the use of higher amounts of linear polymeric material in the composition is not precluded, e.g., amounts
15 such that the linear polymer constitutes 70 or 80%, or even as much as 90%, by weight of the combined polymer and aminoplast.

20 Any suitable means may be employed for incorporating the linear polymer into the amidogen-aldehyde aminoplast. For example, a modified aminoplast may be prepared by first mixing together the
25 amidogen compound, linear polymer and aldehyde and effecting simultaneous condensation between the mixed reactants in the presence or absence of addition agents, for instance condensation catalysts, fillers,
30 other natural or synthetic resinous materials, solvents or diluents. Alternatively, we may add the linear polymer to a partial reaction product of an amidogen compound and an aldehyde, and effect
35 further reaction between the components. Or, we may first partially react the linear polymer with an aldehyde, add the resulting partial reaction product to a partial reaction product of an amidogen com-
40 pound and an aldehyde, and then co-react the mixed partial reaction products. Or, we may react the linear polymer with an excess of an aldehyde, add an amidogen compound to the resulting reaction mass
45 and effect further reaction between the components. Still other ways may be employed in producing a modified amidogen-aldehyde aminoplast in which the linear polymer is chemically bound in
50 the resin molecule. These reactions may be effected under alkaline, neutral or acid conditions and under a variety of time, temperature and pressure conditions. The temperature of the aforementioned reactions may vary from room temperature, in
55 certain cases, to the reflux temperature of the reactants at reduced, atmospheric or superatmospheric pressure. The reactants may be dissolved or dispersed in a suitable liquid medium, if desired, during the
60 reaction.

Any suitable aldehyde may be employed as a reactant with the amidogen compound or with the linear polymer in producing
65 an aldehyde-reaction product thereof.

We prefer to use formaldehyde, e.g., aqueous solutions of formaldehyde. Paraformaldehyde, hexamethylenetetramine, or other compounds engendering formaldehyde also may be employed. In
70 certain cases other aldehydes, e.g., acet-aldehyde, propionaldehyde, butyraldehyde, acrolein, methacrolein, croton-aldehyde, octaldehyde, benzaldehyde, furfural, or mixtures thereof, or mixtures
75 of formaldehyde (or compounds engendering formaldehyde) with such other aldehyde or aldehydes, may be employed. The choice of the aldehyde is dependent upon such factors as, for instance, the
80 particular properties desired in the finished product and economic considerations.

The linear polymer or an aldehyde-reaction product thereof, e.g., a methylol
85 derivative of the linear polymer, or a mixture of the linear polymer and an aldehyde-reaction product thereof, may be incorporated, if desired, into the heat-curable amidogen-aldehyde aminoplast at any suitable stage of the manufacture of
90 a moulding, coating, impregnating, laminating or other composition therefrom. For example, the modifier may be dry or wet blended with the amidogen-aldehyde resin (e.g., a melamine-formaldehyde resin), a filler, (e.g. alpha-cellulose, or wood flour), a mould lubricant (e.g., zinc stearate), and, if desired,
95 a curing catalyst (e.g., phthalic anhydride, tetrachlorophthalic anhydride, ammonium chloride, oxalic acid, acetic acid, phosphoric acid, diammonium phthalate, diammonium hydrogen phosphate, diammonium ethyl phosphate,
100 ammonium silicofluoride, a melamine fluosilicate, a melamine fluoborate, melamine pyrophosphate, chloroacetamide or succinic acid). Thereafter the mixture is worked on hot rolls to cause at least some of the linear polymer or aldehyde-reaction product thereof to coreact or intercondense with the amidogen-aldehyde aminoplast. During
105 such working, the cure of the heat-curable or potentially heat-curable composition is advanced to a desired stage. The resulting sheet is then broken and ground to produce a moulding composition. If necessary, the substantially
110 homogeneous moulding compound may be heated further prior to moulding in order to advance the reaction still further and to stiffen the flow of the compound during moulding.
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Liquid compositions may be produced, for instance, merely by dissolving the amidogen-aldehyde aminoplast and the modifier in a suitable mutual solvent. For example, in the case of water-soluble,
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125
130

alcohol-soluble or water- and alcohol-soluble urea-formaldehyde, melamine-formaldehyde and urea-melamine-formaldehyde resins, the liquid composition 5 may be prepared merely by admixing with such a solution a linear polymer modifier, or an aldehyde-reaction product thereof, or a mixture of the two, which also is 10 soluble in the same solvent or mixture of solvents, or which can be made soluble therein by the addition of another solvent, e.g., acetone.

In order that those skilled in the art may better understand how the present 15 invention may be carried into effect, the following examples are given by way of illustration and not by way of limitation. All parts and percentages are by weight unless otherwise stated. The term "plasticity value" used in these examples is 20 the thickness of a disc obtained in a flow test of the type described at the bottom of page 177 in "Chemistry & Industry," Vol. 56, 1937.

25 EXAMPLE 1.

The linear polymeric material used in this example was produced by reaction of 800 parts of epsilon-caprolactam and 400 30 parts of ammonia. This material was a crude linear polymer containing some unreacted caprolactam. It was a soft, light tan wax. It was heated to 120° C. to free it of ammonia, after which it was heated with an aldehyde, specifically 35 formaldehyde, as follows:

	Parts
Linear polymer - - - - -	20
Aqueous formaldehyde (approx. 37% HCHO) - - - - -	10

40 were heated together until the polymer dissolved, yielding a clear, amber-coloured, slightly viscous solution, which was then heated for several minutes near its boiling point. The resulting solution 45 was clear at room temperature. Upon heating a sample at 90° C. to dryness a resinous material was obtained. The solution of the reaction product of the linear polymer and formaldehyde congealed 50 after standing for several hours at room temperature. After re-dispersing and cooling, the pH of the reaction mass was 9.2.

EXAMPLE 2.

55 Same as Example 1 with the exception that about 5 parts of aqueous 0.5N HCl was added along with the 20 parts of linear polymer and 10 parts of aqueous formaldehyde. A reaction product similar to that of the product of Example 1 60 was obtained. The pH of the cooled solution was 8.7.

EXAMPLE 3.

One hundred and thirty-four (134)

parts of the same linear polymer (which 55 had been heated to 120° C.) as was used in Examples 1 and 2 was extracted (leached) with benzene by heating the benzene-treated polymer on a hot plate, 70 filtering off the benzene-insoluble polymer, and washing it with benzene. The yield of the dried residue (benzene-insoluble polymer) was 85 parts. The filtrate was concentrated on a steam bath, 75 yielding 44 parts of a liquid which crystallised when seeded with a small amount of epsilon-caprolactam. The crystalline solid was mostly unreacted epsilon-caprolactam. When the residue was triturated 80 in water, it dispersed in the form of a fine solid which, on drying, organised itself as a gel.

A portion of the dried, benzene-insoluble polymer was used as follows:

	Parts
Linear polymer - - - - -	20
Aqueous formaldehyde (approx. 37% HCHO) - - - - -	20

were heated together to and at the reflux 90 temperature of the mixed reactants for a total of 10 minutes. The polymer dissolved in the aqueous formaldehyde. Upon cooling the reaction mass to room temperature a crystalline mushy product 95 having a pH of 8.3 was obtained. A sample, which had been heated at 105° C. to yield a film, could be indented by a sharp implement but was somewhat tough and was unaffected by water.

Upon adding water to a sample of the 100 solution of the initial reaction product while cooling, it precipitated. When a concentrated sodium hydroxide solution was added to another sample it produced 105 little change in the cold, with no liberation of ammonia, but attacked the reaction product on warming.

The main portion of the reaction mass was heated under reflux at boiling temperature for an additional 2 hours with 110 little external change in its appearance. Samples of the aqueous reaction product were heated on a melting-point bar at different temperatures with the following results:

115 130° C.: A slightly cloudy melt was obtained, which congealed to a cloudy resin.
160° C.: A clear melt initially was produced. This melt 120 formed a tough material that could be drawn hot into threads.
190°—215° C.: The hot mass could be drawn hot into threads, 125 after which it turned brown and solidified.

EXAMPLE 4.

Same as Example 3 with the exception that 30 parts of aqueous 10% formic acid was added along with the linear polymer and aqueous formaldehyde. The solution was clear after heating for 10 minutes to and at the reflux temperature of the mass. The pH of the solution on cooling was 8.1. The cold reaction mass was a crystalline mush. The addition of water to a small sample, while cooling, did not cause solution of the insoluble material. When a solution of sodium hydroxide was added to another sample, it precipitated an agglomerated mass without the liberation of any ammonia.

When the main reaction mass was heated under reflux at boiling temperature for an additional 2 hours, there was little external change.

EXAMPLE 5.

The linear polymer used in this example was prepared by heating together under reflux for 45½ hours equal molar proportions of epsilon-caprolactam and monoethanolamine. The resulting reaction mass was distilled to remove volatile material under a pressure of about 2 mm. at a temperature of to 250° C. The residual polymer constituted about 74% of the starting reactants. It was a cream-coloured, soft wax which had an intrinsic viscosity of 0.17 and partly melted at 119° C. The polymer was assumed to have an average molecular weight of 513 with a total of five reactive amido and amino groups. It was used in forming an aldehyde-reaction product thereof as described below:

	Parts	Approx. Molar Ratio
Linear polymer - -	200.0	1
Aqueous formaldehyde (approx. 37% HCHO)	158.0	5
MgO - - - -	0.25	

were heated together in a reaction vessel fitted with a sweep stirrer and reflux condenser. Heating was continued at a gradually increasing temperature up to 140° C., at atmospheric pressure and with agitation, for 3½ hours. After heating for about 2 hours under reflux the free formaldehyde in the reaction mixture, originally calculated as being 16.3%, was reduced to 6.4%. At the end of the 3½ hour heating period, the apparatus was fitted up for vacuum distillation and heating under reduced pressure was continued for another 30 minutes to concentrate the reaction product. The yield of the product amounted to 225 parts.

Other aldehyde-reaction products of the

linear polymers identified under Examples 1, 3 and 5 are produced by 65 using, instead of aqueous formaldehyde, equivalent amounts of other aldehydes, e.g. acetaldehyde, acrolein, methacrolein, furfural, butyraldehyde and others such as have been mentioned hereinbefore by 70 way of illustration. The reaction between the aldehyde and the crude or purified linear polymer may be carried out under acid, alkaline or neutral conditions, or initially under alkaline conditions (pH 75 above 7.0) and finally under acid conditions (pH below 7.0), and at temperatures ranging, for example, from room temperature up to the melting or boiling 80 point of the mixed reactants or the boiling point of solutions or dispersions of the dissolved or dispersed reactants.

EXAMPLE 6.

	Parts
Melamine-formaldehyde resin*	487 85
Resin of Example 5 - - -	163
Alpha-cellulose (60 mesh) - -	350
Mould lubricant specifically zinc stearate - - - - -	10

*NOTE: This resin was a dry, heat- 90 curable material obtained by reaction of melamine and formaldehyde in the ratio of 1 mole of the former to 2 moles of the latter.

The above ingredients were blended 95 together in a mixing unit for 1½ hours, the lumps of the Example 5 resin (modifying resin) thereby being broken up to about ¼-inch size. The mixture was further worked on differential rolls having 100 a clearance of 60 mils therebetween. The hot roll (fast roll) was at a temperature of 130° C. at the beginning and 126° C. at the end, while the temperature of the cold roll (slow roll) was 100° C. The 105 modifying resin blended in readily within 1 to 2 minutes. The sheet formed on the cold roll, was transferred to the hot roll in 4 to 6 minutes, and was removed from the latter in 7½ minutes. The sheet 110 showed good plasticity on the rolls and was removed in a single sheet. It was translucent, cream-coloured, and very flexible and strong when cold. The plasticity value (flow mould, 290° F.) was 115 0.041. The sheet was broken and ground in an Abbé cutter through a ½-inch screen to form a moulding compound for test purposes.

A moulded article was produced by 120 moulding a sample of the moulding compound for 5 minutes at 155° C. under a pressure of about 3750 pounds per square inch. The mould shrinkage was 5.6 mils and the after-shrinkage 2.9 mils as com- 125

pared with a mould shrinkage of 6.4 mils and an after-shrinkage of 4.2 mils for a similar melamine-formaldehyde moulding compound containing no modifying resin and which had been cured for 7½ minutes under the same temperature and

pressure conditions. Other pertinent data on moulded articles made from unmodified melamine-formaldehyde moulding compound (A) and from the moulding compound of this example (B) are shown below:

		Moulded Article of	
		(A)	(B)
15	Mould shrinkage, 10 minute cure	6.1 mils	5.0 mils
	After-shrinkage, " " "	5.2 "	2.9 "
	Flexural modulus	1.39 "	1.18 "

EXAMPLE 7.

The formula and procedure were essentially the same as described under Example 6 with the exception that, instead of using 163 parts of the resin of Example 5, there was used about 163 parts of the linear polymer employed in making that resin and the ingredients were blended in the mixer for only 30 minutes instead of 75 minutes. The temperature of the hot roll was 125° C. at the

beginning and 132° C. at the end, while the cold roll was 102° C. at the beginning and 100° C. at the end. The sheet was transferred from the cold roll to the hot roll in 3½ minutes, and was taken off the latter in 5 minutes. The plasticity value was 0.42. Pertinent data on moulded articles made from unmodified melamine-formaldehyde moulding compound (A) and from the moulding compound of this example (C) are shown below:

		Moulded Article of	
		(A)	(C)
40	Mould shrinkage, 10 minute cure	6.1 mils	5.4 mils
	After-shrinkage, " " "	5.2 "	2.1 "
	Mould shrinkage, 15 minute cure	5.7 "	5.6 "
45	After-shrinkage, " " "	7.0 "	2.5 "
	Flexural modulus	1.39 "	1.17 "

EXAMPLE 8.

The linear polymer used in this example and in Example 9 was a reaction product of epsilon-caprolactam and ethanolamine (monoethanolamine). It is a yellow solid having a melting point (softening point) of 178°—180° C. and an intrinsic viscosity of 0.26. This polymer was used in modifying an unfilled melamine-formaldehyde resin as described below:

	Parts
Melamine - formaldehyde resin	
(same as in Example 6) - - -	900
Linear polymer - - - - -	100
Zinc stearate - - - - -	10

The modifier (linear polymer) was reduced in size by passing it through an Abbé mill having a ½-inch screen and then dry blended with the ground melamine resin and zinc stearate. The product was charged to differential rolls having the fast roll (15 r.p.m) at 126° C. and the slow roll at 71° C., the clearance between rolls being 60 mils. After 24 minutes the charge transferred from the cold roll to the hot roll and the dispersion of the modifier then became com-

plete. After 41½ minutes, polymerisation had advanced to the point where the sheet appeared dry and was losing its plastic nature. It was then withdrawn, cooled and ground to granular size. This moulding compound was somewhat stiffer in plastic flow, as evidenced by a higher flow value (0.054) than the compound of the preceding example. When this composition was moulded at 155° C. under a pressure of 3750 pounds per square inch, with a curing period of 10 minutes, the product was highly translucent, indicating a high degree of compatibility of the modifier and parent or primary resin. The modulus of elasticity in flexure was 1.11 as compared with a value of 1.27 for a moulded unplasticised melamine-formaldehyde resin of a similar unfilled type.

EXAMPLE 9.

	Parts
Melamine - formaldehyde resin	
(same as in Example 6) - - -	97.5
Linear polymer (same as in Example 8) - - - - -	97.5
Alpha-cellulose (60 mesh) - - -	350.0
Zinc stearate - - - - -	10.0

The above ingredients were blended together in a mixer for 30 minutes, and the mixture then was milled on differential rolls having a clearance of 60 mils between rolls. The hot or fast roll was at a temperature of 137° C. at the beginning and 134° C. at the end, while the temperature of the cold or slow roll was 97° C. at the beginning and 96° C. at the end. The mixture adhered to the rolls very well and formed cleanly on the cold roll for about 1 to 2 minutes, after which part of the mass was picked up by the hot roll. The transfer to the hot roll was complete in about 4½ minutes. The blend was particularly marked by tenacious adherence to the cold roll until it transferred to the hot roll, but despite this initial tenacity it left the cold roll cleanly. The compound showed good plasticity and sheeting, with no abnormalities, while on the hot roll. After milling for 5½ minutes on the hot roll it was removed therefrom. At this point it was freely plastic, although beginning to show some signs of stiffening. It formed a perfect sheet, which was thin, continuous, leathery and tough when cold. It was translucent, light yellow in colour, and had good uniformity and body texture. The plasticity value (flow mould, 290° F.) was 0.054.

Another sheet was formed in a similar manner, the hot roll being 132° C. at the beginning and 130° C. at the end, while the cold roll was 103° C. at the beginning and 94° C. at the end. The sheet was transferred from the cold to the hot roll in about 4 to 4½ minutes, and was removed from the hot roll after a little over 5 minutes. Its plasticity value was 0.048, and its workability on the rolls and general properties were much the same as the sheet obtained as described in the previous paragraph. This sheet was broken and ground for test purposes as described under Example 6.

When a sample of the resulting moulding compound was moulded around a 1½-inch metal insert, it showed no cracking around the insert after 16 cycles on an insert cracking test. In this test a steel cylinder, 1½ inches in diameter, was moulded as an insert in a plastic part having a diameter of 2 inches. In other words, a ½-inch thick plastic wall surrounded the insert. The part was subjected to a test in which it was heated for 15 hours at 220° F. and then cooled and exposed for 9 hours at room temperature. This cycle was repeated 16 times. In comparison with the aforementioned result a moulded, unplasticised melamine-formaldehyde resin of a similar, filled type showed cracking of the plastic wall

in from 1 to 9 cycles.

When other samples were moulded by heating for periods of 10 and 15 minutes at a temperature and pressure such as was used in moulding the compound of Example 6, the compounds showed good plastic flow during moulding, and yielded hard, well-cured moulded articles having an after-shrinkage only slightly higher than that of the moulded articles of Example 7.

EXAMPLE 10.

The linear polymer used in this example was obtained by heating 1000 parts of epsilon-caprolactam and 500 parts of ammonia under pressure in an autoclave for 24 hours at 200° C.

		Parts	
Melamine - formaldehyde resin			
(same as in Example 6)	- -	488	85
Linear polymer	- -	162	
Alpha-cellulose (60 mesh)	- -	350	
Zinc stearate	- -	10	

were blended together in a mixer for 30 minutes, and the resulting blend then was milled on differential rolls as described in preceding examples. The temperature of the fast or hot roll was 125° C. both at the beginning and at the end, while that of the slow or cold roll was 90° C. at the beginning and 105° C. at the end. The sheet, which formed mostly on the cold roll at the beginning of milling, later transferred in part to the hot roll. After cutting, the transfer to the hot roll was complete in 4 to 5½ minutes. The sheet was removed from the hot roll after about 6 minutes. It came off the roll quite cleanly. It was about ¼ inch thick, cream-coloured, translucent, of uniform texture and quite strong. The plasticity value was 0.042. The sheet was broken and ground for test purposes as described under Example 6.

The compound yielded hard, well-cured moulded articles which showed good plastic flow during moulding. Although the after-shrinkage was slightly higher than that of the moulded articles of Example 9, samples of the compound which were moulded around a 1½-inch metal insert showed no cracking around the insert after 16 cycles on an insert cracking test such as that described under Example 9.

EXAMPLE 11.

Same as Example 6 with the exception that 487 parts of urea-formaldehyde resin (heat-curable urea-formaldehyde resin) is used instead of 487 parts of the heat-curable melamine formaldehyde resin of that example. A well-plasticised moulding compound is obtained, which yields hard, well-cured moulded articles that

show good flow characteristics during moulding at temperatures of the order of 150° C. under pressure of about 2000—3000 pounds per square inch.

- 5 Instead of replacing all of the melamine-formaldehyde resin of Example 6 with a urea-formaldehyde resin, we may substitute only part, e.g., from 10 to 90%, of the melamine resin with a urea resin.

- 10 Likewise, in other examples hereinbefore given the melamine formaldehyde resin of the individual example may be replaced in whole or in part with a urea-formaldehyde resin or with other amidogen-aldehyde resins, numerous examples of which are herein given.

EXAMPLE 12.

- 20 A partial reaction product of melamine and formaldehyde is prepared by heating together under reflux for 30 minutes 126 parts of melamine and 244 parts of aqueous formaldehyde (approx. 37% HCHO). To the resulting partial reaction product 25 is now added 45 parts of a linear polymer obtained by reaction of ammonia and epsilon-caprolactam as described under Example 10, and the linear polymer is inter-condensed into the melamine-formaldehyde partial reaction product by 30 heating the mass under reflux for 1½ hours. The resulting inter-condensation product is used in liquid compositions for laminating paper, canvas and other 35 fibrous sheet materials in the same general manner as hereinbefore described. This syrupy reaction product also may be used in the production of moulding compositions of both the filled and unfilled 40 types. The introduction of the linear polymer into the amidogen-aldehyde aminoplast in this manner (or as described in the example which follows) has the advantage that cured moulded and laminated articles having somewhat better 45 colour are obtained than when the polymer is merely brought into contact with the aminoplast by physical admixture during compounding of a moulding composition or by dissolving the polymer and 50 the aminoplast in a mutual solvent.

EXAMPLE 13.

- A co-reacted amidogen-formaldehyde resin modified with a polymeric reaction 55 product of epsilon-caprolactam and ammonia was also prepared for incorporation into paper through the medium of a paper beater.

	Parts
60 Melamine - - - - -	89
Aqueous formaldehyde (approx. 37% HCHO) - - - - -	198
Linear polymer* - - - - -	100

*NOTE: This polymer was prepared by heating 800 parts of epsilon-caprolactam and 400 parts of anhydrous ammonia in an autoclave at 200° C. After discharging the excess ammonia, the reaction product was heated under reduced pressure to remove unreacted epsilon-caprolactam and other volatile matter. The temperature was taken to 200° C. at 6 mm. pressure. The yield of polymer residue, which was a hard, tough resin when cold, was 70% of the crude reaction product that was subjected to vacuum distillation.

The linear polymer and aqueous formaldehyde were first heated together under reflux for 20 minutes to effect reaction therebetween. After cooling, the melamine was added and heating was continued to cause co-reaction between the melamine and the linear polymer-formaldehyde reaction product. After heating for 35 minutes at 83°—98° C. and a pH of 7.7 to 7.1, a clear, somewhat hydrophobic syrup was obtained. Twenty-five (25) parts of the cooled syrup was dissolved in 78 parts of water and 6.7 parts of concentrated hydrochloric acid. The resulting solution (acid resin solution) was aged for more than one week.

Paper pulp was disintegrated and treated in an experimental paper beater. To the 1% suspension of paper fibres, the above acid resin solution was added to provide 6% of resin solids based on the fibre, and the mixture of fibre stock and resin was agitated for about 30 minutes. Hand sheets were made from the resin-treated paper stock and tested. The dry and wet tensile strengths of these sheets were, respectively, 32.4 and 7.0 pounds per inch as compared with dry and wet tensile strengths of 24.4 and 0.6 pounds per inch for sheets similarly made but which contained no resin.

POST FORMABLE LAMINATES.

The property of formability in a laminate increases its versatility and its potential applications widely. In the decorative laminate field, wherein laminates utilising a melamine-formaldehyde resin as a binder for the laminæ excel, there has long been need for a laminating composition which would make possible the production of post-formable laminated articles. In unmodified form melamine-resin laminates show poor post-forming properties.

The technique used in commercial practice for post-forming laminates involves a short heating period of about 1 to 2 minutes at fairly high temperatures, e.g., 150° to 200° C. or higher, followed

immediately by forming in a die under a low pressure of the order of 5 to 100 pounds per square inch. For heating purposes an oven, infrared lamps or high-frequency heating means are used. Dies may be constructed of wood or metal without expensive finishing. In order properly to be considered "post-formable," laminates must be formable under these conditions. In addition, for a given thickness of laminate, a radius of curvature at least equal to the thickness of the laminate should be possible.

We have discovered that the modified amidogen-aldehyde resinous materials of this invention, and especially the modified melamine-formaldehyde resins, are particularly adapted for use in the production of post-formable laminates. In such compositions the linear polymers obtained by reaction of epsilon-caprolactam with ammonia, especially those having an average molecular weight of the order of 350 or 400 to 600 or 650, seem to be more satisfactory than those produced by reaction of epsilon-caprolactam with a primary or secondary amine or alkanolamine and of the same general order of average molecular weight. However, both classes of linear polymers readily dissolve in the usual amidogen-aldehyde laminating resin solvents (e.g., alcohol, mixtures of water and alcohol, or mixtures of water and ethylene glycol ethyl ether) and, when necessary, can be decolourised in solution, e.g., with a decolourising carbon. For these applications the amount of linear polymer modifier may be varied as desired or as conditions may require, e.g., from about 20 to 60% modifier to from about 20 to 40% of melamine-formaldehyde, urea-formaldehyde or other amidogen-aldehyde resinous composition, more particularly from about 25 to 40% modifier to from about 75 to 60% of amidogen-aldehyde resin, these percentages being by weight. The solvent may be varied in amount in order to produce a liquid composition of the desired viscosity and penetrating characteristics.

EXAMPLE 14.

A liquid impregnating solution was prepared from the following:

	Parts
Linear polymer* (polymeric reaction product of ammonia and epsilon-caprolactam) - - -	75
Melamine - formaldehyde resin (same as Example 6) - - -	225
Denatured ethyl alcohol - - -	50
Water - - - - -	150

*NOTE: This linear polymer was a purified material and had an average molecular weight of about 580.

Strips of 6.7 oz. canvas duck were dipped in the above solution and were then dried for 15 minutes at 115° C. The non-fibrous content of the dried strips was 54%, and a small test sample lost 3.9% of its weight on being heated for 10 minutes at 150° C. An assembly of 5 such sheets having the direction of the weave alternating was pressed for 30 minutes at 150° C. under a pressure of 1000 pounds per square inch. The resulting panel was well-formed, translucent and very slightly yellow. Strips sawed from this canvas-base laminate were heated for 1 minute in an oven at 215° C., removed and quickly bent through 90° over a 1/2-inch radius using a simple wooden die. The cooled piece conformed to the shape of the die and did not straighten out in the course of one year. The bent portion was strong and free from cracks. In marked contrast, a similar panel containing unmodified melamine - formaldehyde resin broke sharply at the bend.

EXAMPLE 15.

The procedure of Example 14 was repeated using the following solution:

	Parts
Linear polymer (same as in Example 14) - - -	150
Melamine - formaldehyde resin (same as in Example 6) - -	150
Denatured ethyl alcohol - -	60
Water - - - - -	140

After a drying period of 15 minutes at 120° C. the non-fibrous content of the dried strips was 55%, and a small sample showed a volatile loss of 5%. Infrared lamps were substituted for the oven heating, and a section of laminate was heated 1 minute to a temperature within the laminate of 150° C. It could then be bent around radii as small as 1/8 inch with only microscopic craze lines appearing.

EXAMPLE 16.

The linear polymer employed in this example was a reaction product of ethanolamine and epsilon-caprolactam, and was the same as that used in Examples 8 and 9.

	Parts
Linear polymer (same as in Examples 8 and 9) - - -	75
Melamine - formaldehyde resin (same as in Example 6) - -	225
Ethylene glycol monoethyl ether	123
Water - - - - -	123

Canvas duck was impregnated with the above solution and dried as in Example 15. The non-fibrous content of the dried

strips was 63%, and a small sample showed a volatile loss of 8.6%. A laminate produced as described under Example 14 was dark in colour but otherwise good. After heating for from 30 to 45 seconds in an oven at 225° C., strips of the panel could be bent without fracture around a $\frac{1}{2}$ -inch radius through 90°.

EXAMPLE 17.

10 This example illustrates the production of a paper-base laminate using a modified amidogen-aldehyde resin of this invention as a binder for the laminæ.

15 Paper was impregnated with the solution of Example 14. The impregnated

paper was dried for 10 minutes at 115° C. The non-fibrous content of the dried paper was 50%, and a small sample lost 3.5% of its weight when heated for 10 minutes at 150° C. An assembly comprising 15 20 superimposed sheets of the impregnated paper was pressed for 30 minutes at 150° C. under a pressure of 1000 pounds per square inch. Although the colour was slightly yellow, the surface appearance, translucency and mechanical properties were all good. The results of tests on this panel in comparison with a panel similarly made from unmodified melamine-formaldehyde resin are shown 30 below:

Panel Produced From
Unmodified Resin Modified Resin

35	Per cent water absorbed after immersion for 24 hours in water at 25° C. - - -	0.8	0.7
	Dynstat flexural strength p.s.i. - - -	1500	1900
	Dynstat angle, degrees - - -	7	8
	Dynstat impact strength, ft. lbs. - - -	13	26
	Flexural modulus ($\times 10^6$) - - -	1.90	1.74

40 It will be understood, of course, by those skilled in the art that our invention is not limited to the specific compositions or to the particular procedures given in the above illustrative examples. Thus, 45 instead of the specific linear polymers employed in the examples we may use, depending, for instance, upon the particular amidogen-aldehyde reaction product which is being modified and the particular use intended for the modified product, any other linear polymer of the kind 50 described in the first three paragraphs of this specification, or formaldehyde- or other aldehyde-reaction products of such linear polymers, or mixtures (in any proportions) of such polymers and aldehyde-reaction products thereof.

The preferred polymers are those having an average molecular weight not 60 higher than, say, 1000 or 1200, more specifically those having an average molecular weight within the range of about 400 to about 600 or 650. The lower-molecular weight polymers are more 65 readily dissolved in alcohol or in mixtures of alcohol and water with obvious advantages, especially in the preparation of liquid coating, impregnating, adhesive, laminating and similar compositions 70 wherein a relatively inexpensive, inert volatile solvent is desired. It may here be mentioned that the linear polymers used in practising this invention that have average molecular weights of the 75 order of 400 to 500 or 600 often yield cloudy solutions upon the addition of

water. However, when such polymers are added to aqueous solutions of an amidogen-aldehyde resin, specifically an aqueous solution of a melamine-formaldehyde resin, solutions of improved clarity 80 are surprisingly obtained.

Our invention is operative with reaction products of an aldehyde, specifically formaldehyde, and any monomeric amidogen compound containing at least two 85 aldehyde-reactable amino or amido or amino and amido groupings, that is to say, any monomeric amidogen compound containing at least two amidogen groupings each having at least one hydrogen 90 atom (preferably two hydrogen atoms) attached to the amidogen nitrogen atom.

As amidogen-aldehyde aminoplasts we prefer to use heat-curable or potentially 95 heat-curable resinous reaction products of ingredients comprising a polyaminotriazine (e.g., melamine) and formaldehyde, or comprising urea, melamine (or other polyaminotriazine) and formaldehyde. However, heat-curable or potentially heat-curable urea-formaldehyde, thiourea-formaldehyde and thiourea-melamine-formaldehyde resinous reaction products also may be employed. 105 Dimethylol urea, alkyl ethers thereof, polymethylol melamines (more particularly mono-, di-, tri-, tetra-, penta- and hexamethylol melamines) and alkyl ethers thereof may be used. Examples of 110 other amidogen compounds which may be reacted with an aldehyde to provide the primary product which is modified in

accordance with the present invention are: methylurea, phenylurea, phenylthiourea, allylurea, guanylurea, guanylthiourea, dicyandiamide, guanidine, biguanide, diaminodiazines, guanazole and other diaminotriazoles, ammeline or ethylenediamine. Numerous examples of aldehydes that may be reacted with the amidogen compound have been mentioned hereinbefore. These amidogen-aldehyde aminoplasts are prepared, in general, in accordance with technique well known to the art. The molar ratio of aldehyde to amidogen compound, depending, for instance, upon the particular amidogen compound employed, may vary, for example, from 0.35 to 2.0 moles thereof for each aldehyde-reactable amidogen grouping in the amidogen compound. Similar proportions of formaldehyde or other aldehyde may be used in preparing the aldehyde-reaction product of the linear polymer.

Dyes, pigments and opacifiers may be incorporated into the compositions of this invention to alter the visual appearance and the optical properties of the finished product. If needed, mould lubricants may be added to facilitate moulding of the heat-convertible (heat-hardenable) moulding compositions. Fillers (e.g., alpha-cellulose, asbestos, mica, or wood flour) may be incorporated to obtain a wide variety of moulding compounds and moulded articles adapted to meet particular conditions. Curing agents, examples of which have been given hereinbefore, also may be added. Other effect agents also may be incorporated as desired or as conditions may require.

Thermosetting (heat - hardenable) moulding compositions comprising a heat-curable or potentially heat-curable amidogen-aldehyde aminoplast which has been modified, specifically plasticised or softened and/or toughened as herein described, may be moulded into a variety of shapes under heat and pressure, more particularly at temperatures of the order of 100° to 200° C., preferably from approximately 120° or 130° to 170° or 180° C. The plasticised compositions show good plastic flow during moulding. Moulded articles of manufacture comprising the moulded, heat-hardened moulding compositions produced in accordance with our invention have a good surface finish, show no evidence of "bleeding" plasticiser and have other improved properties such as have been mentioned or indicated (for instance, in many of the examples) hereinbefore.

The modified amidogen-aldehyde aminoplasts of our invention are especially suitable for use in producing postform-

able laminated articles comprising superimposed sheets of fibrous material such as paper, glass cloth, or cloth formed of silk, wool, cotton or rayons, or cloths produced from synthetic fibres, e.g., fibres of nylon, polyacrylonitrile (or copolymers of acrylonitrile), vinyl chloride-acrylonitrile copolymers or vinyl chloride-vinylidene chloride copolymers. In such structures the sheets are impregnated and bonded together with a thermoset product of reaction of ingredients comprising an aldehyde, specifically formaldehyde, and a monomeric amidogen compound of the kind aforementioned, which reaction product is modified (plasticised or softened and/or toughened) with a modifier of the kind previously described. In such cases, the linear polymeric material employed has an average molecular weight of not more than 2000 and constitutes at least 5%, preferably at least 20%, but not more than 50 or 60% by weight of the total amount of aminoplast and modifier. The scope of the invention also includes articles of manufacture comprising the post-formable laminated article which has been post-formed to a desired shape. Our invention also includes within its scope the method which comprises impregnating fibrous sheet material with liquid compositions of the kind herein described, drying the impregnated material, superimposing the dried sheets, bonding the superimposed sheets together under heat and pressure (e.g., under such conditions of heat and pressure as aforementioned with reference to the production of a moulded article) thereby to obtain a laminated sheet article, and deforming the laminated article while hot to a desired shape.

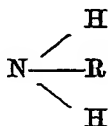
Our modified amidogen - aldehyde aminoplasts are also useful as adhesives, as components of surface protective compositions, as additives to paper pulp in making a wet-strength paper and for numerous other purposes. The modified amidogen-aldehyde aminoplasts of our invention, both filled and unfilled, have a wide variety of applications other than those hereinbefore described. In the filled compositions the amount of filler (examples of which previously have been given) may be widely varied depending, for example, upon the particular filler employed and the intended use of the filled composition or product. Thus, the amount of filler may constitute, for instance, from a few per cent (e.g., from 2 to 5 or 10%) up to 50 or 60%, or even as much as 70 or 80% in some cases, by weight of the combined weight of filler and modified amidogen-aldehyde amino-

plast.

Our co-pending specification No. 651,338 of earlier date claims a thermosetting moulding or laminating composition comprising a fusible amino-aldehyde resin plasticised with a compatible preformed high molecular polyamide resin of predominantly linear structure which is soluble in alcohol or aqueous alcohol and which either has a softening point below 155° C. or is used with a compatible plasticiser so as to bring the softening point below 155° C. We make no claim herein to what is claimed in said specification.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A composition comprising a product of reaction of (a) an aldehyde and (b) a monomeric amidogen compound (as hereinbefore defined), said reaction product being modified with a nitrogenous compound which is different from the compound of (b) and which is either (1) a linear polymeric reaction product of (A) ϵ -caprolactam and (B) a compound represented by the general formula



wherein R represents hydrogen or an alkyl or monohydroxyalkyl radical, the ingredients of (A) and (B) being employed in the ratio of 1 mole of the former to not less than 1 mole of the latter; or (2) an aldehyde reaction product of (1); or (3) a mixture of (1) and (2).

2. A composition as claimed in Claim 1 in which the ingredients of (A) and (B) are employed in the ratio of 1 mole of the former to from 1—20 moles of the latter.
3. A composition as claimed in Claim 1 or 2 in which the aldehyde of (a) and/or (2) is formaldehyde.
4. A composition as claimed in any of Claims 1 to 3 in which the amidogen compound of (b) is urea.
5. A composition as claimed in any of Claims 1 to 3 in which the amidogen compound of (b) is melamine.

6. A composition as claimed in any of Claims 1 to 4 in which the compound of (B) is ammonia.

7. A composition as claimed in any of Claims 1 to 5 in which the compound of (B) is monoalkanolamine.

8. A composition as claimed in Claim 7 in which the monoalkanolamine is monoethanolamine.

9. A composition as claimed in any of Claims 1 to 8 in which the said linear polymeric reaction product has an average molecular weight of not more than 2,000.

10. A composition as claimed in Claim 9 in which the molecular weight of the linear polymeric reaction product is 400 to 1200.

11. A composition as claimed in any of Claims 1 to 10 in which the nitrogenous modifier constitutes 5—50% by weight of the combined weight of the modifier and the reaction product of (a) and (b).

12. A composition as claimed in any of the preceding Claims in which the reaction product of (a) and (b) and the nitrogenous modifier are incorporated under heat.

13. A composition as claimed in any of the previous Claims in which the reaction product of (a) and (b) is intercondensed with the nitrogenous modifier.

14. A method for the production of shaped laminates which comprises impregnating fibrous sheet materials with the composition according to any of the preceding Claims, drying the impregnated materials, superimposing the dried sheets, bonding the superimposed sheets together under heat and pressure to obtain a laminated sheet material and deforming the said laminated material while hot to the desired shape.

15. Shaped laminated articles prepared by the method according to Claim 14.

16. A composition when prepared by a process substantially as described in any of Examples 6—12.

17. Resin-treated pulp sheets when prepared by a process substantially as described in Example 13.

18. Resin-bonded laminates when prepared by a process substantially as described in any of Examples 14—17.

Dated this 19th day of April, 1949.

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